Sub-Doppler optical frequency reference at 1.064 μm by means of ultrasensitive cavity-enhanced frequency modulation spectroscopy of a C_2HD overtone transition

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Using our cavity-enhanced frequency modulation technique, we obtained the saturated signal of the weakly absorbing gas C_2HD for the $P(5)$ line of the $(\nu_2 + 3\nu_3)$ overtone band at 1.064 μm. An absorption sensitivity of 1.2×10^{-10} (1.8×10^{-12}/cm) has been obtained. The absolute frequency of the line center is established (within ± 2.6 kHz) with respect to a doubled Nd:YAG laser/I_2 frequency reference. The short-term stability, limited by the available signal-to-noise ratio, currently is 1×10^{-11} at 1 s, improving to 5×10^{-13} at 1000 s. The measured pressure-broadening rate is 34.7(0.8) kHz/mTorr (260 ± 6.1 kHz/Pa). Selection of slow molecules gave a linewidth four times narrower than the room-temperature transit-time limit.

Owing to its merits of high energy efficiency, compact size, long lifetime, and intrinsic low noise, the all-solid-state diode-laser-pumped Nd:YAG laser (NPRO) is a promising candidate for precision scientific measurements. Using this 1.064-μm source, some Doppler-limited absorptions have been studied with CO_2 (Ref. 1) and C_2H_2 (Ref. 2) molecules, and sub-Doppler absorption by Cs molecules has been used for laser stabilization.[3] A frequency-doubled Nd:YAG laser has been well stabilized to hyperfine transitions in I_2 near 532 nm.[4] Here we report what to our knowledge is the first observation of a submegahertz resonance located at 1.064 μm, obtained by applying our newly developed cavity-enhanced FM spectroscopy to a weak molecular overtone transition in C_2HD.[5,6] In addition to some linewidth studies, we have frequency stabilized a Nd:YAG laser onto this reference and established its absolute frequency.

Molecular overtones extend molecular rovibronic transitions well into the visible range, providing useful combs of resonances while inheriting the same slow decay and approximate kilohertz linewidths as their infrared fundamentals. With a number of suitable molecules one can expect to offer hundreds of lines and to have broad spectral coverage. These overtone transitions are thus ideal for ultrahigh-resolution spectroscopy and for building densely populated visible frequency standards. The main problem with the very weak absorption strengths associated with the overtone transitions can be readily overcome by placement of the sample molecules inside a high-finesse cavity.[7,8] With our new FM technique we frequency modulate the laser beam at exactly the cavity free-spectral-range splitting (FSR) frequency so that the cavity treats the carrier and sidebands in precisely the same manner; thus the maximum cavity finesse can be utilized without a corresponding large frequency-to-amplitude noise conversion.[5,6] After heterodyne detection the transmitted FM triplet will produce a useful signal only when one component (the central carrier in the present experiment) is phase shifted by the molecular dispersion.

Figure 1 shows our experimental setup for high-resolution spectroscopy of line $P(5)$ in the $(\nu_2 + 3\nu_3)$ overtone band of $^{12}C_2HD$. Synthesized HCCD gas (81%/19% HCCD/HCCH by integration of the ^{1}H NMR spectrum, ~55% chemical purity by a residual gas analyzer) is placed inside a cavity with a FSR of 319.689 MHz. One mirror is flat; the other has a 1-m radius of curvature. The intracavity beam waist is ~0.410 mm, dictating the room-temperature transit-time limit of 270 kHz FWHM.[9] An empty cavity finesse of 9300 was measured by a cavity-field ring-down method. A high finesse value helps to increase the detection sensitivity and build up adequate intracavity power for saturation of the weakly absorbing gas. The measured linear absorption coefficient is 6.7×10^{-7}/(Torr cm), in good agreement with the available band-strength data.[10] In a plain gas cell that is the length of our cavity 10 mTorr (1.33 Pa) of pure HCCD would attenuate the 1.064-μm input beam by ~0.3 parts in 10^6 (0.3 ppm). The present cavity has a resonant transmission efficiency of 40.5%, which decreases by 770 ppm near the Doppler profile peak (a contrast of 0.2%). Tuning onto the saturation resonance increases the maximum transmission by 46 ppm, corresponding to a saturation depth of 6% (11% saturation depth was obtained at a lower pressure). The cavity input power was varied from 75 to 2.5 mW. By locking with a rf sideband technique we narrowed the laser's full energy spectrum and efficiently coupled it into the cavity. Electro-optical modulator 2 (EOM2) produced the locking FM sidebands at 4 MHz. An acousto-optic modulator (AOM) and the NPRO's internal piezoelectric transducer (PZT) served as the frequency servo transducers. The servo gain was sufficient to provide a low frequency-noise density of $0.30\ \mathrm{Hz}/\sqrt{\mathrm{Hz}}$, corresponding to a 0.28-Hz laser linewidth relative to the cavity.[11] Phase modulation of the laser beam at the free-spectral-range

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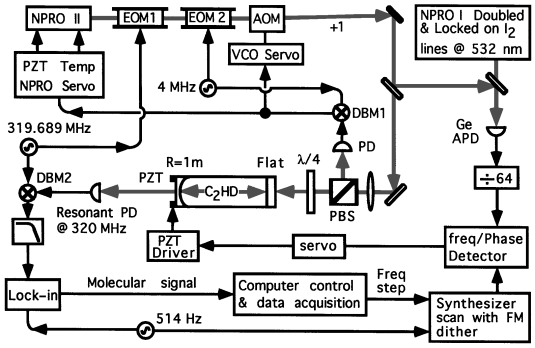

Fig. 1. Spectrometer setup for precision scanning of the C_2HD overtone resonance at 1.06 μm. Our sensitive detection concept is shown by EOM1 phase modulating the laser beam at the cavity free-spectral-range frequency, providing (frequency-) noise-immune heterodyne detection of the transmitted light. PZT's, piezoelectric transducer; $\lambda/4$, quarter-wave plate; PBS, polarizing beam splitter; APD, avalanche photodiode; DBM, double-balanced mixer; PD, photodiode; VCO, voltage-controlled oscillator.

frequency was generated by resonantly coupled EOM1 and detected in cavity transmission by an InGaAs p-i-n diode in a resonant rf tank circuit. Subsequent phase-sensitive demodulation yielded the molecular dispersion signal. To establish an absolute frequency mark and reference for scanning, another NPRO was frequency doubled and locked onto an I_2 reference at 532 nm. The heterodyne beat signal between the two NPRO's (after digital phase division by 64) was phase locked to a synthesizer. To improve S/N and baseline stability, we modulated the cavity around the molecular resonance by an FM dither on the synthesizer and used an audio lock-in for signal recovery. The same synthesizer was frequency stepped by a computer to force the cavity NPRO to scan out the molecular resonance. Signal averaging over many scans ($\sim$1 min each) was available with the long-term stability of the NPRO I_2 system in the sub-100-Hz domain.

Figure 2 shows a typical scan of the overtone resonance. The gas pressure was 13 mTorr. Our line-shape model is based on Wahlquist's modulation-broadening formalism for a dispersion signal.[12] The fit residual is shown with 5$\times$ magnification. With the saturated absorption measured at 0.33 ppm, we achieved a S/N of 240 (normalized for a 1-s time constant), corresponding to a detection sensitivity of 1.2×10^{-10} (1.8×10^{-12}/cm). This is twice the calculated shot-noise level, with 120 μW on the detector and a modulation index of 0.2 for the 319.7-MHz FM sidebands. The linewidth (FWHM) of 854(6) kHz includes broadening by pressure, power, and molecular transit time through the laser beam.

Subsequently we experimented with the pressure broadening at some fixed input powers as well as the power broadening at some fixed gas pressures. At low pressures such as 3 mTorr we obtained a saturation level of $\sim$0.8 with the maximum available input power of 75 mW. By knowing the saturation at each pressure we were then able to find the power-broadening contribution to the linewidth and make corresponding corrections. Figure 3 shows our measured pressure broadening and the result after the saturation broadening has been removed, indicating a pressure-broadening (FWHM) coefficient of 34.7 $\pm$ 0.8 MHz/Torr. We note that earlier results of pressure broadening on other C—H bond molecules such as CH_4 (Ref. 13) and C_2H_2 (Ref. 6) yielded 32.6 $\pm$ 1.2 and 29.8 $\pm$ 0.1 MHz/Torr, respectively. These large broadening coefficients may be due in part to the sensitivity of saturated absorption to velocity-changing collisions. The zero-pressure zero-intensity extrapolated linewidth was 290 $\pm$ 7 kHz, very near the value set by the transit time. We can summarize these results with the following expression for the saturation intensity: $I_{\mathrm{sat}} = 6103(\Gamma_T + 34.7P)^2$ W/mm^2, where Γ_T is the FWHM (in megahertz) associated with transit time and P is the pressure (in Torr). The equivalent saturation power in the free-flight regime is 117 W inside, reduced to 62-mW input by the cavity enhancement of 1880. Our measurement of the line center versus pressure also indicates a pressure shift of approximately +250 ($\pm$20%) Hz/mTorr.

Linewidth narrowing is offered by slow molecules since the natural lifetime of the overtone transition is almost 300 times longer than our current transit time, thereby reducing the transit-time broadening.[14] In our 2-mTorr sample gas the mean-free path of molecules is $\sim$30 times longer than the transverse field dimension, thereby creating the so-called transit-time regime. The cavity input power was reduced 30 times, from our maximum available power, to 2.5 mW. A low power is necessary so that the low Rabi frequency leads to appreciable saturation for only the slowest molecules. Figure 4 shows a resonance with a linewidth of $\sim$70 kHz, without correction for the modulation broadening by a 46-kHz peak-to-peak dither of the cavity. This is four times narrower than

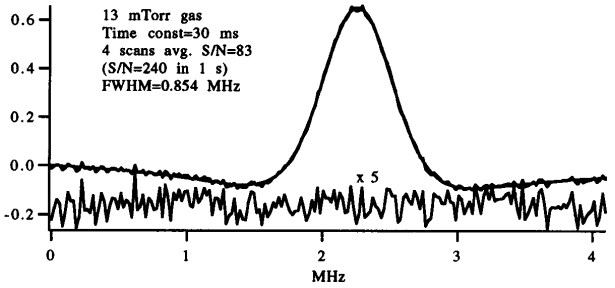

Fig. 2. Frequency scan of the resonance line shape and overlaid theoretical fit based on Wahlquist's modulation-broadening formalism. Fit residuals (5$\times$) are shown by the lower curve.

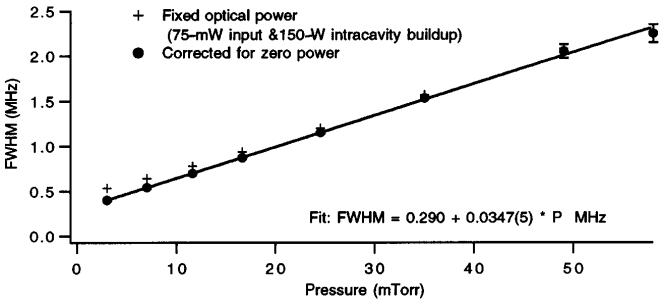

Fig. 3. Pressure-broadening measurements of line $P(5)$ in the $^{12}C_2HD$ ($\nu_2 + 3\nu_3$) overtone band.

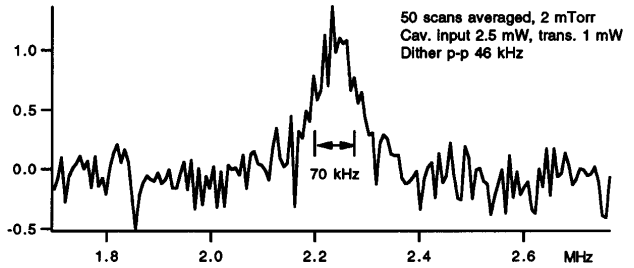

Fig. 4. With low power and gas pressure, slow molecules give a line width of four times below the transit limit.

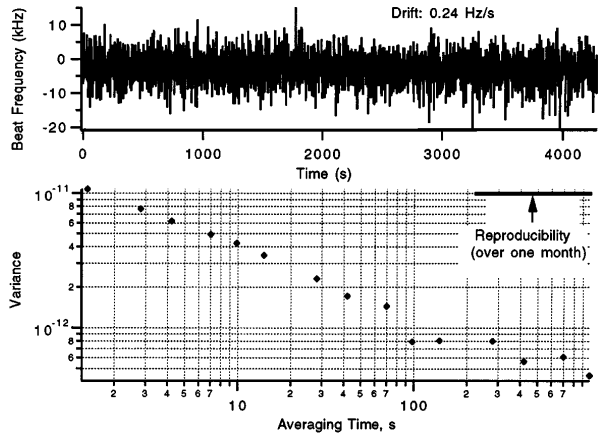

Fig. 5. Time record of the beat frequency between the two NPRO's, one locked on the C_2HD overtone transition, the other frequency doubled and locked on an I_2 reference at 532 nm, which is 5252.2254 ± 0.0026 MHz lower. The Allan variance is calculated from these data.

that set by the room-temperature transit-time limit and is limited mainly by the relatively high pressure (2 mTorr). With our computer-based scan system we are ready to explore the limit of our detection sensitivity with much lower pressure. By increasing our intracavity mode size and observing slow molecules we should be able to probe the hyperfine and recoil structures and enter a qualitatively new regime of ultrahigh-resolution spectroscopy of molecular overtone transitions.

To test the quality of this C_2HD overtone resonance as an optical frequency standard at 1.064 μm, we locked the NPRO/cavity system onto the line and measured the heterodyne beat against the known NPRO/I_2 reference system.[4] We used second harmonic detection on our lock-in to obtain a third-derivative discrimination signal that was integrated and then fed onto the PZT of the C_2HD cavity. In Fig. 5 the counted beat frequency versus time shows a drift of ~860 Hz/h. NPRO I (after frequency doubling) was locked on I_2:$R(56)$ 32–0, component a_{10}.[4,6] With the mean value of the beat frequency between the two lasers at 5252.2254 ± 0.0026 MHz, we determined the absolute frequency of line $P(5)$ in the $(\nu_2 + 3\nu_3)$ band of $^{12}C_2HD$ to be 281 635 363.961 MHz ± 20.2 kHz. At 1-s averaging we obtained a frequency noise of ±3.1 kHz, in perfect agreement with that calculated from the S/N available at 1.064 μm. The corresponding Allan variance of $\sigma_y = 1.1 \times 10^{-11}/\sqrt{\tau}$ is approximately two times worse than that of the 633-nm He–Ne/I_2 system. However, even in these first experiments the day-to-day reproducibility of ±2.6 kHz (1 part in 10^{11}) is actually better. By increasing the modulation index at 320 MHz and using a higher-finesse cavity (a 60,000-finesse cavity is under construction) we should be able to improve the S/N by a factor of 10. This should produce a frequency noise of ±0.3 kHz at 1-s averaging.

In summary, we have demonstrated a valuable optical frequency reference at 1.064 μm with a molecular C_2HD overtone transition, using our sensitive detection method of noise-immune cavity-enhanced optical heterodyne molecular spectroscopy. Slow molecules have been optically selected, and a fourfold linewidth reduction was observed. Ultrahigh-resolution spectroscopy of molecular overtone transitions with the ability to resolve hyperfine structures is being actively pursued.

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